

(12) **UK Patent Application** (19) **GB** (11) **2 324 097** (13) **A**

(43) Date of A Publication **14.10.1998**

(21) Application No **9807599.7**

(22) Date of Filing **08.04.1998**

(30) Priority Data

(31) **19715037** (32) **11.04.1997** (33) **DE**

(71) Applicant(s)

BASF Aktiengesellschaft
(Incorporated in the Federal Republic of Germany)
D-67056 Ludwigshafen, Federal Republic of Germany

(72) Inventor(s)

Wolfgang Ruff
HansUlrich Reisacher
Joachim Jesse
Erika Beßler

(74) Agent and/or Address for Service

J Y & G W Johnson
Kingsbourne House, 229-231 High Holborn, LONDON,
WC1V 7DP, United Kingdom

(51) INT CL⁶

C09D 11/02 , C09B 67/08

(52) UK CL (Edition P)

C4A AC14 AC7 AK

(56) Documents Cited

None

(58) Field of Search

UK CL (Edition P) C4A

INT CL⁶ C09B 67/08 , C09D 11/02

Data-base: WPI

(54) Abstract Title

Pigment preparation in pellet form

(57) A pigment preparation in pellet form is composed of organic pigment particles coated with an acidic resin comprising a mixture of free resin acid and resin soap. The pigment preparation is useful for pigmenting printing inks.

GB 2 324 097 1

Pigment preparations in pellet form based
on organic pigments

The present invention relates to novel pigment preparations
5 in pellet form based on coated organic particles.

The invention further relates to the production of these pigments
and to their use for pigmenting printing inks.

- 15 It is known to coat organic pigments with acidic resins
(EP-A-263 951, 311 560 and 313 360). The coating with the resin
is frequently effected by adding the resin in the form of an
aqueous alkali metal resinate solution to a neutral or alkaline
aqueous pigment suspension and then acidifying the mixture to
20 precipitate the resin as resin acid onto the pigment particles,
although the addition of dissolved metal salts will convert the
resin acid into the resin soap to some extent. The pigments are
then isolated as powder by filtration and drying.
- 25 The resin-coated pigments, comprising up to 50% or more by weight
of resin, have advantageous color properties, such as high gloss,
high transparency and, despite the resin content, a color
strength similar to that of the resin-free pigments, and also
favorable rheological properties, and are usually used for
30 producing printing inks, especially letterpress and offset
printing inks.

Compared with pulverulent pigment preparations, pigment pellets
cause much less of a dust nuisance and are free flowing and are
35 therefore finding increasing interest. They are advantageously
produced by collecting the pigment, if desired after
pretreatment, as water-moist filter cake, which is then forced
through a pelletizing die. The subsequent drying can take place,
for example, continuously on a belt dryer. The pellets obtained
40 in this way are customarily 0.3-0.8 cm in thickness and from
0.5-2 cm in length.

However, it is difficult to pelletize pigments having a high
resin content, especially a high coat weight of resin acids,
45 since the filter cake will usually no longer have the requisite
plasticity.

It is an object of the present invention to remedy the aforementioned defects and to provide pigment preparations having advantageous application properties.

5 We have found that this object is achieved by a pigment preparation in pellet form, wherein the organic pigment particles are coated with an acidic resin comprising a mixture of free resin acid and resin soap.

10 The present invention also provides a process for producing this pigment preparation, which comprises coating the pigment particles, suspended in an aqueous medium, with a mixture of resin acid and resin soap, collecting the resin-coated pigment on a filter means, pelletizing the moist filter cake via a
15 pelletizing die and drying the pellets.

Lastly, the present invention provides for the use of this pigment preparation for pigmenting printing inks.

20 The essential feature of the pigment pellets of the present invention is that the organic pigment particles are coated with a resin acid/resin soap mixture.

It is surprising that organic pigments coated with the resin
25 mixture of the present invention are highly suitable for pelletization.

In general, this resin mixture comprises from 20 to 90 mol% of resin soap and from 10 to 80 mol% of resin acid.

30 Suitable resin soaps are in particular the zinc salt and the calcium salt of the acidic resin. It is also possible to use mixtures of these salts.

35 Preferred compositions of the resin mixture are 20-75 mol% of resin soap and 25-80 mol% of resin acid in the case of the zinc soaps and 30-80 mol% of resin soap and 25-70 mol% of resin acid in the case of the calcium soaps.

40 According to the present invention, the acidic, i.e. carboxyl-bearing, resin can be a natural, semisynthetic or synthetic resin, which preferably has an acid number ≥ 100 .

Examples of particularly suitable resins are acrylate, polyester
45 and phthalate resins and especially rosins such as rosin itself and its well-known derivatives, e.g. dimerized, polymerized, hydrogenated and disproportionated rosin and the reaction

products with maleic acid and fumaric acid.

The resin content of the pigment preparations of the present invention is generally within the range from 20 to 55% by weight,
5 preferably within the range from 30 to 50% by weight.

The higher the resin content is, the higher the resin soap content should be. In the case of resin contents $\geq 50\%$ by weight, the acidic resin therefore preferably comprises $\geq 40 \text{ mol\%}$ of resin
10 soap.

The pigment can be any organic pigment in finely divided form. Examples of suitable pigment classes are monoazo, disazo, anthraquinone, anthrapyrimidine, quinacridone, quinophthalone,
15 diketopyrrolopyrrole, dioxazine, flavanthrone, indanthrone, isoindoline, isoviolanthrone, perinone, perylene, phthalocyanine, pyranthrone, and thioindigo pigments and mixtures thereof.

Of particular interest are unlaked azo pigments, especially
20 β -naphthol and naphthol AS pigments as monoazo pigments and bisacetoacetarylides, disazopyrazolone and especially diaryl yellow pigments as disazo pigments.

The following pigments of the individual classes are mentioned by
25 way of example:

- monoazo pigments: C.I. Pigment Brown 25;
C.I. Pigment Orange 1, 5, 36 and 67;
C.I. Pigment Red 1, 2, 3, 112, 146,
30 170 and 184;
C.I. Pigment Yellow 1, 2, 3, 73, 74, 65 and 97;
- disazo pigments: C.I. Pigment Orange 16 and 34;
35 C.I. Pigment Red 144 and 166;
C.I. Pigment Yellow 12, 13, 14, 17, 83, 106, 113, 114, 126, 127, 174, 176 and 188;
- 40 - anthraquinone pigments: C.I. Pigment Yellow 147;
C.I. Pigment Violet 31;
- anthrapyrimidine pigments: C.I. Pigment Yellow 108;
45
- quinacridone pigments: C.I. Pigment Red 122 and 202;
C.I. Pigment Violet 19;

- quinophthalone pigments: C.I. Pigment Yellow 138;
- dioxazine pigments: C.I. Pigment Violet 23 and 37;
- 5 - flavanthrone pigments: C.I. Pigment Yellow 24;
- indanthrone pigments: C.I. Pigment Blue 60 and 64;
- 10 - isoindoline pigments: C.I. Pigment Orange 69;
C.I. Pigment Red 260;
C.I. Pigment Yellow 139 and 185;
- isoindolinone pigments: C.I. Pigment Yellow 109, 110 and 173;
- 15 - perinone pigments: C.I. Pigment Orange 43;
C.I. Pigment Red 194;
- perylene pigments: C.I. Pigment Black 31 and 32;
20 C.I. Pigment Red 123, 149, 178, 179,
190 and 224;
C.I. Pigment Violet 29;
- phthalocyanine pigments: C.I. Pigment Blue 15, 15:1, 15:2,
25 15:3, 15:4, 15:6 and 16;
C.I. Pigment Green 7 and 36;
- pyranthrone pigments: C.I. Pigment Orange 51;
C.I. Pigment Red 216;
- 30 - thioindigo pigments: C.I. Pigment Red 88;
- C.I. Pigment Black 1 (aniline black);
- 35 - C.I. Pigment Yellow 101 (aldazine yellow).

The pigment preparations of the invention may include further additives which are customary for the respective pigment. In the case of azo pigments, for example, known coupling assistants such as surfactants, long-chain fatty acids and amines and
40 crystallization inhibitors such as the coupling product of bisdiazotized 4,4'-diaminobiphenyl-2,2'-disulfonic acid and acetoacet-m-xylylidide (EP-A-263 951) may be present. These additives can be present in the pigment preparations in an amount
45 of up to 15% by weight.

The pigment pellets of the invention can advantageously be

obtained by the production process of the invention by coating the pigment particles, suspended in a preferably alkaline aqueous medium, with the resin acid/resin soap mixture, then collecting the resin-coated pigment on a filter means, pelletizing the moist filter cake via a pelletizing die and drying the pellets.

It was found that the resin acid/resin soap ratio depends not only on the pH of the pigment suspension, but also on the metal used for soap formation.

10

For instance, for example in the case of C.I. Pigment Yellow 13 being coated with partially hydrogenated rosin, approximately the following molar ratios of resin acid/resin soap are generally found in the resin-coated pigment as a function of the pH when the preferred calcium and zinc soaps are used in at least equivalent amounts to the acidic resin:

	pH	Resin acid/calcium soap	pH	Resin acid/zinc soap
20	8	0/100	6	0/100
	7.5	10/90	5.5	15/85
	7	25/75	5	55/45
	6.5	45/55	4.75	90/10
25	6	65/35		
	5.5	85/15		
	5	90/10		

There are therefore two ways to coat the pigment particles in a controlled manner with whichever is the desired resin acid/resin soap mixture.

Way (a) comprises using the metal salt used to form the resin soap in an amount which corresponds to the amount of resin to be converted into resin soap, and adjusting the pH of the pigment suspension so that the metal salt is converted quantitatively.

Way (b) comprises using an excess of metal salt and adjusting the pH of the pigment suspension so that the metal salt is converted only to the extent which corresponds to the desired ratio of resin soap to resin acid.

The process of the present invention is advantageously carried out as follows:

45

The aqueous pigment suspension (which, for example in the case of azo pigments, can advantageously be the suspension obtained in

pigment synthesis) is initially rendered alkaline, i.e. adjusted to a pH which is generally within the range from 7 to 13, preferably within the range from 9 to 12, and then admixed with an alkaline aqueous solution of the acidic resin (alkali metal resinate solution). The pH of the suspension following addition of the resin is customarily within the range from 9 to 12.

The suspension is then heated to about 90-100°C. This heat treatment generally takes from 15 to 60 min.

10

An aqueous solution of the metal salt used for soap formation (e.g. zinc sulfate or calcium chloride) is then added and, if desired after further heating for from about 15 to 60 min, the pH is adjusted with an acid, preferably dilute hydrochloric acid, to customarily 3-8, preferably 4.5-7.

If desired after further brief heating or stirring, the resin-coated pigment is filtered off, the moist filter cake is pelletized and the pellets are dried.

20

The pellet-form pigment preparations of the present invention are advantageously useful for pigmenting printing inks, including especially letterpress and offset printing inks, and are notable in this application for advantageous application properties, especially good gloss, high color strength, good viscosity and ready dispersibility in the application medium.

Examples

30 I) Production of pigment preparations according to the invention

Examples 1 to 7

First, C.I. Pigment Yellow 13 was synthesized as follows:

35

The tetrazocomponent was prepared by admixing a suspension of 28 g of 3,3'-dichloro-4,4'-diaminobiphenyl (3,3'-dichlorobenzidine) in 600 ml of 1 N hydrochloric acid with 15.3 g of sodium nitrite at 0°C. Excess nitrous acid was then removed with amidosulfuric acid, after which the solution was filtered off.

40

The coupling component was prepared by dissolving 47.6 g of acetoacet-2,4-dimethylanilide in 305 ml of 1.5 N sodium hydroxide solution.

45

The coupling vessel was charged with 310 ml of 0.5 N acetic

acid. Sufficient coupling component was then added to obtain a pH of 5.0. Thereafter the tetrazo component and the rest of the coupling component were added simultaneously while the pH was maintained at 4.5 and the temperature at 20°C.

5

After the coupling reaction had ended, a pH of 11 was set with 17 ml of 25% strength by weight sodium hydroxide solution, at which point a tetrazo component prepared by tetrazotization of 1.2 g of 4,4'-diaminobiphenyl-2,2'-disulfonic acid in 16 ml of 1 N hydrochloric acid at 0°C with 0.5 g of sodium nitrite was added.

10

Following complete reaction of the tetrazonium salt, a solution of x g of partially hydrogenated rosin (Staybelite® E-Resin, from Bercules) in x₁ ml of 0.3 N sodium hydroxide solution was added to the pigment suspension with stirring.

15

Following 30 minutes' heating at 100°C, y g of the metal salt M, dissolved in y₁ ml of water, were added with stirring.

20

Following a further 15 minutes of heating at 100°C and subsequent cooling back to 80°C, the pH of the suspension was adjusted to the value W by addition of 1 N hydrochloric acid.

25

Following brief subsequent stirring and cooling to 50°C, the resin-coated pigment was filtered off. The filter cake was forced with a manual press through a pelletizing die (hole diameter 0.4 cm), which presented no problem in any of the examples. The pellets were then dried at 60°C.

30

Further details of these examples and their results are recited in Table 1.

35

40

45

Table 1

Ex.	x g of resin	x ₁ ml of water	y g	Metal salt M	y ₁ ml of H ₂ O	pH	Pigment pellets		
							Resin content in % by weight	Metal content in % by weight	Ratio of resin acid/resin soap in mol%
1	52.5	650	19.3	ZnSO ₄ ·7H ₂ O	200	5	40	Zn: 1.9	56/44
2	52.5	650	7.7	ZnSO ₄ ·7H ₂ O	100	6	40	Zn: 1.2	73/27
3	52.3	650	13.1	CaCl ₂ ·2H ₂ O	150	7	40	Ca: 2.0	25/75
4	52.3	650	13.1	CaCl ₂ ·2H ₂ O	150	6	40	Ca: 1.0	62/38
5	64.2	790	16.0	CaCl ₂ ·2H ₂ O	150	6	45	Ca: 1.0	66/34
6	78.5	970	19.7	CaCl ₂ ·2H ₂ O	200	6.5	50	Ca: 1.8	44/56
7	95.8	1180	23.1	CaCl ₂ ·2H ₂ O	230	6.5	55	Ca: 2.0	43/57
COMP	42.3	5.20	-	-	-	4.5	35	-	100/0

II) Evaluation of application of properties

5 To enable the application properties to be evaluated,
 printing inks were prepared by stirring, in each case, 7.5 g
 of the resin-coated pigment into 42.5 g of a varnish composed
 of 40% by weight of rosin-modified phenolic resin, 27% by
 weight of refined linseed oil and 33% by weight of PKWF 6/9
 mineral oil (from Haltermann) and then dispersing with a
 10 Dispermat Dissolver (toothed disk diameter 0.3 cm) at 12,000
 rpm at 50°C for 10 min. The predispersed paste was then
 ground at a nip pressure of 10 bars on an SDY 200 three-roll
 mill (from Bühler).

15 Color strength:

The color strength is reported in terms of coloring
 equivalents (CE) and was determined via the white reduction
 of the respective printing ink with a white paste. To this
 20 end, 0.5 g of printing ink was mixed with 10 g of a 40% by
 weight pigment content white paste on a JEL 25/53 disk
 grinder (from Engelsmann) by 4 x 35 revolutions.

25 The comparative preparation with pigment COMP, coated only
 with resin acid, was assigned the CE value 100 (standard). CE
 values < 100 mean a higher color strength than that of the
 standard, CE values > 100 accordingly a lower color strength.

30 Gloss:

The gloss was measured on a 100 μ drawdown of the respective
 printing ink on cardboard (dried at 25°C for 74h) using a
 micro-Tri-gloss meter (from Byk-Gardner) at a measuring angle
 of 60°.

35 Viscosity:

The viscosity of the respective printing ink was determined
 with a Rheo Stress RS 100 rheometer (from Haake).

40 The results of these tests are summarized in Table 2.

45

Table 2

5	Printing inks with the pigment of Ex.	Color strength CE value	Gloss	Viscosity [Pa·s]
	1	103	76	84
	2	101	76	79
10	3	98	61	56
	4	98	77	57
	5	105	77	53
	6	116	74	61
	7	130	77	55
15	COMP	100	76	32

20

25

30

35

40

45

CLAIMS

1. A pigment preparation in pellet form, wherein organic pigment particles are coated with an acidic resin comprising a mixture of free resin acid and resin soap.
- 5 2. A pigment preparation as claimed in claim 1, wherein the resin mixture comprises from 20 to 90 mol% of resin soap and from 10 to 80 mol% of resin acid.
3. A pigment preparation as claimed in claim 1 or 2, wherein the resin soap is the zinc or calcium salt of the
10 acidic resin or a mixture of these salts.
4. A pigment preparation as claimed in any of claims 1 to 3, wherein the acidic resin is a natural, semisynthetic or synthetic resin having an acid number ≥ 100 .
5. A pigment preparation as claimed in any of claims 1 to
15 4, wherein the acidic resin is a resin based on rosin.
6. A pigment preparation as claimed in any of claims 1 to 5, comprising from 20 to 55% by weight of the resin mixture.
7. A pigment preparation as claimed in any of claims 1 to 6, comprising an unlaked azo pigment as organic pigment.
- 20 8. A pigment preparation as claimed in claim 1 and substantially as hereinbefore described and exemplified.
9. A process for producing a pigment preparation as claimed in any of claims 1 to 8, which comprises coating organic pigment particles, suspended in an aqueous medium,
25 with a mixture of free resin acid and resin soap, collecting the resin-coated pigment on a filter means, pelletizing the moist filter cake via a pelletizing die and drying the pellets.

10. A process as claimed in claim 9, wherein the pigment particles are coated with the mixture of resin acid and resin soap by (a) using the metal salt used to form the resin soap in an amount which corresponds to the amount of resin to be
5 converted into resin soap, and adjusting the pH of the pigment suspension so that the metal salt is converted quantitatively, or (b) using an excess of metal salt and adjusting the pH of the pigment suspension so that the metal salt is converted only to the extent which corresponds to the
10 desired ratio of resin soap to resin acid.

11. A process as claimed in claim 9 carried out substantially as hereinbefore described or exemplified.

12. The use of a pigment preparation as claimed in any of claims 1 to 8 or produced by a process as claimed in any of
15 claims 9 to 11 for pigmenting printing inks.

13. Printing inks containing pigment preparations as claimed in any of claims 1 to 8.



Application No: GB 9807599.7
Claims searched: 1-13

Examiner: S.I.Ahmad
Date of search: 30 June 1998

Patents Act 1977
Search Report under Section 17

Databases searched:

UK Patent Office collections, including GB, EP, WO & US patent specifications, in:

UK Cl (Ed.P): C4A(AC, AK)

Int Cl (Ed.6): C09B-67/08 ; C09D-11/02

Other: Data-base; WPI

Documents considered to be relevant:

Category	Identity of document and relevant passage	Relevant to claims
	No relevant document	

X	Document indicating lack of novelty or inventive step	A	Document indicating technological background and/or state of the art.
Y	Document indicating lack of inventive step if combined with one or more other documents of same category.	P	Document published on or after the declared priority date but before the filing date of this invention.
&	Member of the same patent family	E	Patent document published on or after, but with priority date earlier than, the filing date of this application.